PATENT SPECIFICATION

(11) 1 603 122

1 603 122

(21) Application No. 23918/77 (22) Filed 8 June 1977
(23) Complete Specification filed 24 May 1978
(44) Complete Specification published 18 Nov. 1981
(51) INT CL³ C07C 161/00; A01N 41/12; C07F 9/24
(52) Index at acceptance
C2C 200 220 221 224 225 227 22Y 291 29Y 30X 30Y 311 313 31Y 323 326 32Y 332 338 339 350 364 365 36Y 385 510 514 51Y 520 523 526 620 660 662 694 699 805 80Y AA SB SC SU
A5E 222 224 239 241 243 246 252 253 256 257 258 269 270 271 273 274 278 503 504 506 507 A
C2P 2L25A 2L26B 2L26D 2L26F 7 B1 B

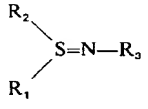
(72) Inventors KENNETH EDWARD WHITAKER and PETER KIRBY

(54) PESTICIDAL SULPHILIMINE DERIVATIVES

(71) We, SHELL INTERNATIONALE RESEARCH MAATSCHAPPIJ B.V., a company organised under the laws of The Netherlands, of 30 Carel van Bylandtlaan, The Hague, The Netherlands, do hereby declare the invention for which we pray that a patent may be granted to us and the method by which it is to be performed, to be particularly described in any by the following statement:—

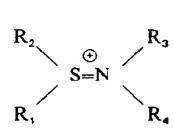
The present invention relates to a method of controlling or eradicating pests using sulphilimine derivatives, to compositions containing those derivatives, to novel sulphilimine derivatives and to processes for preparing such sulphilimine derivatives.

The Applicants have found certain sulphilimine derivatives to have interesting pesticidal properties. In particular the Applicants have found, as appears hereinafter, that such derivatives may show both insecticidal and particularly herbicidal activity. Accordingly the present invention provides a method of controlling or eradicating pests at a locus which comprises applying to the pest or to the locus of the pest a pesticidally effective amount of a sulphilimine derivative of formula:



(I)

or



(II)

wherein each of R_1 and R_2 independently represents an optionally substituted alkyl, cycloalkyl, aryl, aralkyl, alkaryl or sulphonamido group;

R_3 represents (a) a hydrogen atom when at least one of R_1 and R_2 does not represent a lower alkyl or phenyl group, (b) a trihaloacetyl group, (c) a cyano group when at least one of R_1 and R_2 represents an at least disubstituted phenyl group, (d) a phenyl group containing up to 4 substituents, (e) an optionally substituted benzene sulphonyl group provided that, when, in a derivative of formula I, this is a para-tosyl group, at least one of R_1 and R_2 represents a phenyl group having at least one non-alkyl substituent, or one of R_1 and R_2 represents a haloalkyl group and the other represents an alkyl group and when the benzene sulphonyl group has an optionally substituted amino substituent in the para position, at least one of R_1 and R_2 does not represent a lower alkyl or phenyl group, or (f) a group $—C(Q)=C(CN)_2$ when at least one of R_1 and R_2 represents a substituted phenyl group, (g) a group

$$-P(OR_8)(OR_9) \quad \text{or} \quad \text{(h) a group } -C(=X)-Y$$

in which

Q represents a hydrogen atom, a cyano group or an optionally substituted alkyl group;

X represents an oxygen or sulphur atom;

Y represents a group $-NR_5R_6$ or ZR_7 in which Z represents an oxygen or sulphur atom; each of R_5 and R_6 independently represents a hydrogen atom, or an optionally substituted alkyl, cycloalkyl, aryl, alkaryl, or aralkyl group; and R_7 represents an optionally substituted alkyl, cycloalkyl, aryl, aralkyl, or alkaryl group;

and each of R_8 and R_9 independently represents an optionally substituted alkyl, cycloalkyl, aryl, alkaryl, or aralkyl group;

R_4 represents a hydrogen atom, an optionally substituted alkyl, cycloalkyl, acyl or aryl sulphonyl group;

and A represents an anion.

When used herein, and in the Claims, the term lower alkyl means an alkyl group having up to 4 carbon atoms.

Preferably in the groups represented by Q, R_1, R_2, R_4, R_5, R_6, R_7, R_8 and R_9 in formulae I and II above, the alkyl, alkaryl and aralkyl groups have up to 10 carbon atoms, and the cycloalkyl groups have from 5 to 8 carbon atoms.

Preferred compounds for use in the method according to the present invention are sulphilimine derivatives of formulae I and II above, wherein in formulae I and II each of R_1 and R_2 independently represents an alkyl group optionally substituted by one or more halogen atoms, a benzenesulphonamido which may be substituted by up to 3 alkyl groups, or a cycloalkyl, phenyl, aralkyl or alkaryl group which may be substituted by one or more halogen atoms and/or alkyl, hydroxy, alkoxy, cyano, formyl, nitro, polyhaloalkyl, amino, or mono- or dialkylamino groups or by a benzoyloxy group which may itself be substituted with up to 4 halogen atoms or nitro groups;

R_3 represents (a) a hydrogen atom, (b) a trihaloacetyl group, (c) a cyano group, (d) a phenyl group substituted by one or more halogen atoms, nitro groups, or amino, or mono- or di-alkylamino groups, (e) a benzene sulphonyl group (e') a para-tosyl group provided that at least one of R_1 and R_2 represents a phenyl group having at least one nitro substituent, or (f) a group $-C(Q)=C(CN)_2$ when at least one of R_1 and R_2 represents a phenyl group having at least one nitro substituent, or (g) a group

$$-P(OR_8)(OR_9) \quad \text{or} \quad \text{(h) a group } -C(=X)-Y$$

in which

Q represents a hydrogen atom, a cyano group or an alkyl group optionally substituted by one or more halogen atoms;

X represents an oxygen or sulphur atom;

Y represents a group $-NR_5R_6$ or $-ZR_7$ in which Z represents an oxygen or sulphur atom; each of R_5 and R_6 independently represents a hydrogen atom, an alkyl group optionally substituted by one or more halogen atoms, or a cycloalkyl, phenyl, alkaryl or aralkyl group optionally substituted by one or more halogen atoms and/or one or more alkyl, hydroxy, cyano, formyl, nitro, polyhaloalkyl, amino, or mono- or di-alkylamino groups or by a benzoyloxy group which may itself be substituted by up to 4 halogen atoms or nitro groups; and R_7 represents an alkyl, cycloalkyl, phenyl, alkaryl or aralkyl group optionally substituted by one or more halogen atoms or a haloalkyl group;

and each of R_8 and R_9 independently represents an alkyl, cycloalkyl, alkaryl, or aralkyl group optionally substituted by one or more halogen atoms, or alkyl or nitro groups;

R_4 represents a hydrogen atom, an alkyl or cycloalkyl group, an acyl group of up to 11 carbon atoms, or a benzene sulphonyl group which may be substituted by up to 3 alkyl groups;

and A represents a halide, polyhalide, (thio)carboxylate, cyanide, hydroxide, sulphate, alkylsulphate, hydrogen-sulphate, benzene sulphonate, alkyl- or alkylsubstituted benzene sulphonate, nitrate, phosphate, hydrogen phosphate, carbamate, mono- or dialkyl substituted carbamate, hydrogen carbonate, alkyl sulphonate, chlorate, perchlorate, bromate, perbromate, thiocyanate, tetrafluoroborate or thiosulphonate.

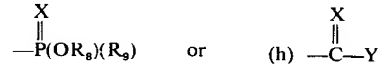
It should be noted that the expression "anion" also includes di- and tri-anions in which case the sulphilimine derivatives used in the method according to the present invention comprise two or three sulphilimine structures.

A preferred class ("class I") of sulphilimine derivatives of formula I above are those in which R_1 is a methyl group; R_2 is a phenyl group substituted by one or more halogen atoms and/or nitro groups; particularly by one halogen atom and one nitro group; and R_3 is a hydrogen atom, for example methyl-(2-nitro-4-chloro-phenyl)sulphilimine.

A further preferred class ("class II") of sulphilimine derivatives of formula I for use in the method according to the present invention are those in which:

R_1 and R_2 both represent phenyl groups; and

R_3 represents a trihaloacetyl group, a phenyl group substituted by up to 3 nitro, trifluoromethyl or methosulphate groups particularly a 2,6-dinitrophenyl group, or one of the groups (g)



(in which Y is $-NR_5R_8$ or $-ZR_7$) and wherein;

R_5 represents a hydrogen atom or one of the groups represented by R_6;

R_6 represents an alkyl group of up to 6 carbon atoms, a cycloalkyl group of from 5 to 8 carbon atoms especially a cyclohexyl group, or a phenyl group optionally substituted with one or two halogen atoms, preferably chlorine or fluorine atoms, or one or two alkyl groups of up to 4 carbon atoms;

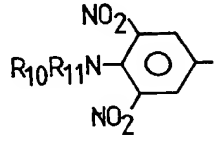
R_7 is an alkyl group of up to 6 carbon atoms for example an ethyl or isopropyl group or a phenyl or benzyl group;

and each of R_8 and R_9 independently represents an alkyl group of up to 6 carbon atoms or an aryl group such as a phenyl group.

Another preferred class ("class III") of sulphilimine derivatives are those of formula I and II in which:

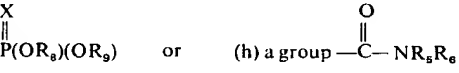
R_1 represents an alkyl group of up to 6 carbon atoms, preferably a methyl group;

R_2 represents a group of formula:



wherein each of R_{10} and R_{11} independently represents an alkyl group of up to 6 carbon atoms, especially a propyl group;

R_3 represents (a) a hydrogen atom, (b) a trihaloacetyl, particularly trichloroacetyl, group, (c) a cyano group, (e) a benzene sulphonyl group optionally substituted by up to 3 alkyl, preferably methyl, groups, or (f) the group $-C(Q)=C(CN)_2$, (g) the group



in which,

Q represents a hydrogen atom, a cyano group, or an alkyl group of up to 6 carbon atoms;

X represents an oxygen or sulphur atom;

R_5 represents a hydrogen atom or a group represented by R_6;

R_6 represents an alkyl group of up to 6 carbon atoms especially a methyl group, or a phenyl group opionally substituted by one or two of halogen atoms, especially chlorine atoms, or alkyl groups of up to 6 carbon atoms;

and each of R_8 and R_9 independently represents an alkyl group of up to 6 carbon atoms or an aryl group, especially a phenyl group;

R_4 represents a hydrogen atom an alkyl group of up to 6 carbon atoms, an acyl group or a benzene sulphonyl group optionally substituted by up to 3 alkyl, preferably methyl, groups;

and A represents a halide, especially a chloride ion, a tetrafluoroborate, or a fluorosulphonate ion, or a benzenesulphonate group optionally substituted by up to 3 alkyl, especially methyl, groups.

Examples of such sulphilimine derivatives are methyl-(3,5-dinitro-4-dipropylaminophenyl)sulphilimine, hydrochloride, the corresponding p-tosyl- and O-mesitylene sulphonyl salts and methyl-(3,5-dinitro-4-dipropylaminophenyl)-N-(N'-methylamido)-sulphilimine.

A further preferred class ("class IV") of sulphilimine derivatives which may be used in the method according to the present invention are those compounds of formula II wherein:

R_1 represents a haloalkyl group of up to 10 carbon atoms, especially a 2-chloroethyl group, or a phenyl group substituted by one or more of halogen atoms, preferably chlorine atoms, alkyl groups of up to 4 carbon atoms, trifluoromethyl, nitro, amino, cyano and formyl groups;

R_2 represents an alkyl group of up to 10 carbon atoms, a phenyl group optionally substituted by one or two halogen atoms or alkyl groups of up to 4 carbon atoms, or (R_2 represents) a benzyl group optionally ring substituted by 1 or 2 halogen atoms and/or alkyl groups of up to 4 carbon atoms;

R_3 represents a hydrogen atom or an alkyl group of up to 10 carbon atoms;

R_4 represents a hydrogen atom, or a benzene sulphonyl group optionally substituted by up to 3 alkyl, preferably methyl, groups;

and A represents a halide, especially a chloride or bromide, a tetrafluoroborate, or a fluorosulphonate ion or a benzene sulphonium ion which may be substituted by up to 3 alkyl, especially methyl, groups.

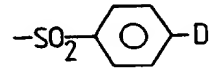
An example of this class of sulphilimine derivative is methyl-(p-nitrophenyl)-sulphilimine, O-mesitylene sulphonic acid salt.

A still further class ("class V") of sulphilimine derivatives useful in the method of the present invention are compounds of formula I wherein:

R_1 represents a haloalkyl group of up to 10 carbon atoms, particularly a 2-chloroethyl group, or a phenyl group substituted by one or more halogen atoms, hydroxy, nitro or 3,5-dinitrobenzoyloxy groups;

R_2 represents an alkyl group of up to 6 carbon atoms, preferably a methyl group;

and R_3 represents a group of formula:



wherein D represents a hydrogen atom or an alkyl group of up to 6 carbon atoms, preferably a methyl group.

An example of this class of compound is methyl-(2-nitro-4-chlorophenyl)-N-(p-tolyl sulphonyl)sulphilimine.

Finally, another preferred class ("class VI") of sulphilimine derivatives are those compounds of formula I wherein;

R_1 represents a methyl group;

R_2 represents a 2-nitrophenyl group or a 2-nitrophenyl group substituted by a halogen, preferably a chlorine, atom; and

R_3 represents a group $—C(Q)=C(CN)_2$ or a group

$$-C(=O)-NHR_6$$

in which Q represents a hydrogen atom, a cyano group or an alkyl group of up to 6 carbon atoms, especially a methyl group, and R_6 represents an alkyl group of up to 6 carbon atoms, particularly a methyl group.

Suitable substituents referred to hereinabove comprise halogen atoms, especially chlorine or fluorine atoms, alkyl, alkoxy, or thioalkoxy groups of up to 6 carbon atoms and aryl or aryloxy groups containing up to 10 carbon atoms.

As mentioned hereinbefore, the sulphilimine derivatives according to the present invention are of interest as pesticides. They are especially of interest as herbicides, exhibiting pre- and/or post-emergence activity. Some sulphilimine derivatives, especially those of class III above also exhibit plant growth regulating properties such as growth depression and thickening of the stems. Sulphilimine derivatives of class VI above wherein R_3 represents a $-C(Q)=C(CN)_2$ group also exhibit insecticidal properties, especially against vetch aphids (*Megoura viciae*) and spider mites (*Tetranychus urticae*).

The present invention further provides pesticidal, particularly herbicidal compositions comprising as active ingredient at least one sulphilimine derivative of formula I or II, as defined above, together with a surface active agent and a carrier (which may itself be the surface active agent), with the exception that when R_3 is a benzene sulphonyl group substituted by a chlorine atom, a nitro or lower alkyl group, at least one of R_1 and R_2 is not an optionally substituted lower alkyl group, or a phenyl, benzyl or sulphonamido group.

Many of the sulphilimine derivatives described above are novel compounds, and accordingly a further aspect of the invention are novel sulphilimine derivatives of formulae I and II as defined above provided that:

(i) when R_3 represents a hydrogen atom, R_1 and R_2 do not both represent 4-fluorophenyl groups, nor both represent 4-chlorophenyl groups, neither R_1 nor R_2 represents a phenyl group or a 4-methylphenyl group, and when one of R_1 and R_2 represents a methyl group the other does not represent an octyl or tetradecyl group.

(ii) when R_3 represents a trihaloacetyl group, (b), R_1 and R_2 do not both represent lower alkyl groups, and if one of R_1 and R_2 represents a phenyl group, the other does not represent a methoxyphenyl group.

(iii) when R_3 represents a phenyl group, (d), that group contains from 2 to 4 substituents which are not 2,4- or 3,5-dinitro substituents, and at least one of R_1 and R_2 is not a lower alkyl group.

(iv) when R_3 represents an optionally substituted benzene sulphonyl group, (e), at least one of R_1 and R_2 represents an at least disubstituted phenyl group, other than a 2,4-dichlorophenyl group.

(v) when R_3 represents a group $-C(Q)=C(CN)_2$, (f), and Q represents a cyano group, R_1 and R_2 do not both represent phenyl groups.

(vi) when R_3 represents a group

$$-C(=X)-Y$$

(h), and this group is a lower alkoxycarbonyl group, neither R_1 nor R_2 represents a lower alkyl group.

(vii) when R_3 represents the group

$$-C(=X)-Y$$

(h), and this group is a methoxycarbonyl, ethoxycarbonyl, lower alkylaminocarbonyl, phenylamino carbonyl or phenylaminothioxomethyl group, R_1 and R_2 do not both represent phenyl groups.

(viii) when R_3 represents the group

$$-C(=X)-Y$$

(h), and this is an unsubstituted aminocarbonyl group, at least one of R_1 and R_2 is an at least disubstituted phenyl group.

The sulphilimine derivatives of general formulae I and II above can be suitably prepared by methods known in the art for related compounds.

Suitable starting materials for the preparation of sulphilimines comprise sulphides of the general formula R_1R_2S, wherein R_1 and R_2 have the meaning as hereinbefore defined. In order to obtain the relatively stable sulphilimines according to the present invention it is advantageous to prepare compounds of the formula $R_1R_2S=NH$, which can be reacted further, if necessary to obtain sulphilimines of the general formulae (I) and (II). The compounds of formula $R_1R_2S=NH$ can be conveniently prepared by the following novel routes:

$$R_1R_2S+MsONH_2 \longrightarrow R_1R_2S^{\oplus}—NH_2OMs^{\ominus} \xrightarrow{\text{base}} R_1R_2S=NH$$

or

$$R_1R_2S+TsNClNa \xrightarrow{\text{acid}} R_1R_2S=NTs \xrightarrow{\text{acid}} R_1R_2S^{\oplus}—NH_2OTs^{\ominus} \xrightarrow{\text{base}} R_1R_2S=NH$$

In these reactions Ms represents a mesitylene sulphonyl group and Ts a tosyl group. The reaction between the sulphide and the mesitylene sulphonyl or tosyl-derivative can be suitably carried out in organic solvents such as ethers, ketones or alcohols. It has been found that the use of a small amount of a carboxylic acid, e.g. acetic acid, considerably enhances the speed of the reaction when methanol is used as the solvent. Also aprotic solvents such as dimethylformamide in the presence of acetic acid can be applied successfully especially when the tosyl-derivative is used. The intermediate aminosulphonium salts are obtained in good yields (up to 90%) even from sulphides bearing electronegative groups.

The final liberation of the compounds of formula $R_1R_2S=NH$ is normally achieved quantitatively by reacting the aminosulphonium salts with a base such as aqueous sodium carbonate or by using an anion-exchange resin such as Amberlite IR-410 ("AMBERLITE" is a Registered Trade Mark). In the event of groups R_1 and/or R_2 carrying highly electronegative substituents, O-mesitylene sulphonylhydroxylamine has to be used to obtain the corresponding aminosulphonium salt.

The sulphilimines of the general formula $R_1R_2S=NH$ can be conveniently converted into further sulphilimines. For instance, sulphilimine derivatives of class II can be suitably prepared by reacting diphenylsulphilimines with the appropriate (thio) isocyanate, or a compound of formula YCOCl or a compound of formula

$$Cl—\overset{\overset{X}{\|}}{P}(OR_8)(OR_9).$$

When using a chlorine containing reagent a certain amount of the salt of the diphenylsulphilimine is also formed. It is therefore recommended to use a two-fold excess of the starting sulphilimine.

Sulphilimine derivatives of general formula I wherein R_3 represents a di- or tri-substituted phenyl group such as a 2,6-dinitrophenyl- or a 2,6-dinitro-4-trifluoromethylphenyl group, can be suitably prepared by reacting a sulphilimine derivative of formula $R_1R_2S=NH$ with the appropriate substituted chlorobenzene, the corresponding sulphilimine salt also being formed. Sulphilimine derivatives of class IV can be conveniently prepared by Michael-type condensation reactions of a sulphilimine derivative of formula $R_1R_2S=NH$ with an appropriate cyano-substituted ethylene derivative.

If desired, the sulphilimine derivatives according to formula I can be converted into the corresponding salts, depicted by formula II, by methods known in the art. Under certain conditions, salts according to formula II (sometimes originating from the starting sulphilimine derivatives) are already formed during the preparation of the sulphilimine derivatives.

It is also possible to convert salts according to formula II into salts with different anions by an anion exchange reaction. For instance a chloride derivative can be easily converted into the corresponding iodide derivative by dissolving it in ethanol and adding an excess of an aqueous potassium iodide solution.

The term "carrier" as used herein means a solid or fluid material with which the active ingredient is mixed or formulated to facilitate its application to the plant,

seed, soil or other object to be treated, or its storage, transport or handling. Any of the carrier materials or surface-active agents usually applied in formulating pesticides may be used in the compositions according to the invention, and suitable examples of these are to be found, for example, in British Patent Specification No. 1,293,546. A carrier may itself be the surface active agent.

The compositions of the invention may be formulated as wettable powders, dusts, granules, solutions, emulsifiable concentrates, emulsions, suspension concentrates or aerosols. Wettable powders are usually compounded to contain 25—75% of toxicant and usually contain, in addition to solid carrier, 3—10%w of a dispersing agent, and where necessary, up to 10%w of stabilizer(s) and/or additives such as penetrants or stickers. Dusts are usually formulated as a dust concentrate having a similar composition to that of a wettable powder but without a dispersant, and are diluted in the field with further solid carrier to give a composition usually containing 0.5—10%w of toxicant. Granules are usually prepared to have a size between 0.15 and 1.68 mm, and may be manufactured by agglomeration or impregnation techniques. Generally, granules will contain 0.5—25%w of toxicant and, where necessary, up to 10%w of additives such as stabilizers, slow release modifiers and binding agents. Emulsifiable concentrates usually contain, in addition to the solvent and, where necessary, co-solvent, 10—50%w/v of toxicant, 2—20%w/v of emulsifiers and, where necessary, up to 20%w-v of appropriate additives, such as stabilizers, penetrants and corrosion inhibitors. Suspension concentrates are compounded so as to obtain a stable, non-sedimenting, flowable product and usually contain 10—75%w of toxicant, 0.5—15%w of dispersing agent(s), 0.1—10%w of suspending agents such as protective colloids and thixotropic agents, and, where necessary, up to 10%w of appropriate additives such as defoamers, corrosion inhibitors, stabilizers, penetrates and stickers, and as carrier, water or an organic liquid in which the toxicant is substantially insoluble; certain organic solids or inorganic salts may be dissolved in the carrier to assist in preventing sedimentation or as anti-freeze agents for water.

Aqueous dispersions and emulsions, for example compositions obtained by diluting a wettable powder or an emulsifiable concentrate according to the invention with water, also lie within the scope of the present invention. The said emulsions may be of the water-in-oil or of the oil-in-water type, and may have a thick 'mayonaise'-like consistence.

The compositions according to the invention may also contain other ingredients, for example those mentioned in British Patent Specification No. 1,293,546, and/or other pesticidally active compounds such as insecticides, acaricides, herbicides or fungicides which are compatible with the other ingredients in the composition.

The invention is further illustrated in the following Examples: The structures of the compounds prepared were confirmed by elemental and N.M.R. analysis.

Example 1

Preparation of diphenylsulphilydene-N'-methylurea

Diphenylsulphilimine ($(C_6H_5)_2S=NH$, 2.19 g) and methylisocyanate (0.57 g) were stirred in dry benzene (50 ml) at room temperature for one hour. After evaporation of the solvent, the product was recrystallised from benzene/petroleum ether 40—60 M.p. 143—145°C.

Analysis:

Calculated for $C_{14}H_{14}ON_2S$	:	C 65.1;	H 5.4;	N 10.9%
Found	:	C 64.9;	H 5.2;	N 10.5%

Example 2.

Preparation of diphenylsulphilydene-N'-cyclohexyl thiourea

Diphenylsulphilimine (1.1 g) and cyclohexylisothiocyanate (0.7 g) were refluxed in dry benzene (30 ml) for 15 minutes. The solvent was evaporated from the dark mixture resulting in a pinkish solid which was recrystallised from acetone/petroleum ether 40—60 to give 1.2 g of colourless crystals. M.p. 116—118°C.

Analysis:

Calculated for $C_{19}H_{21}S_2N_2$	:	C 66.7;	H 6.4;	N 8.2%
Found	:	C 66.0;	H 6.7;	N 8.2%

Example 3.

Preparation of diphenylsulphilydene benzyl carbamate

Benzylchloroformate (0.86 g) was added to diphenylsulphilimine (2.19 g) in dry benzene (30 ml) at room temperature. An exothermic reaction occurred and an oil separated which solidified. After filtrate 0.8 g of the sulphilimine hydrochloric salt was obtained. The filtrate was evaporated and the residual oil triturated with acetone/petroleum ether 40—60 to give diphenylsulphilydene benzyl carbamate (0.9 g). M.p. 53.5°C.

Analysis:

Calculated for $C_{20}H_{17}O_2NS$	:	C 71.6;	H 5.4; N 4.2%
Found	:	C 71.5;	H 5.1; N 4.7%

Example 4.

Preparation of diphenyl-N-trichloroacetylsulphilimine

Trichloroacetylchloride (0.91 g) was added to diphenylsulphilimine (2.19 g) in benzene (30 ml). The mixture was stirred at room temperature for 3 hours following the initial exothermic reaction. The hydrochloride salt obtained was filtered off. The solvent in the filtrate was evaporated and the residual oil triturated with petroleum ether 40—60 to provide the product in the form of colourless crystals. M.p. 97—99°C.

Analysis:

Calculated for $C_{14}H_{10}ONSCl_3$	:	C 48.6;	H 2.9; N 4.1%
Found	:	C 48.5;	H 2.9; N 3.9%

Example 5.

Preparation of N-(diethoxyphosphoryl)diphenylsulphilimine

Diphenylsulphilimine (1.1 g) and diethylchlorophosphate (0.43 g) were stirred in benzene at room temperature for 3 hours. The precipitated sulphilimine hydrochloride salt was collected and from the filtrate was a colourless viscous oil obtained (0.85 g).

Analysis:

Calculated for $C_{16}H_{20}O_3NSP$	:	C 57.0;	H 5.9; N 4.2%
Found	:	C 57.8;	H 5.6; N 4.5%

Example 6.

Preparation of N-(2,6-dinitrophenyl)diphenylsulphilimine

Diphenylsulphilimine (1.1 g) and 2,6-dinitrochlorobenzene (0.3 g) were refluxed in benzene (15 ml) for 2 hours. The mixture was filtered when cold off the sulphilimine hydrochloride (0.6 g) and the product desired was obtained as a yellow solid (0.9 g) by evaporation of the filtrate and trituration of the residual oil with petroleum ether 40—60. M.p. 100—102°C.

Analysis:

Calculated for $C_{18}H_{13}O_4N_3S$	:	C 58.8;	H 3.5; N 11.4%
Found	:	C 58.8;	H 3.7; N 11.2%

Examples 7—20.

Following procedures similar to those given in previous Examples, further compounds were prepared; the physical characteristics and analyses are set out in Table 1.

Example 21.

Preparation of (4-dipropylamino-3,5-dinitrophenyl)-methylsulphilimium mesitylenesulphonate

4-Dipropylamino-3,5-dinitrophenyl-methylsulphide (3.13 g) and O-mesitylene sulphonylhydroxylamine (2.15 g) were stirred in methylene chloride (30 ml) at room temperature for 3 hours. Ether (50 ml) was added, and the fine yellow crystalline salt filtered off (3.9 g). M.p. 174—176°C.

Analysis:

Calculated for $C_{22}H_{24}O_7N_4S_2$	:	C 50.0;	H 6.1;	N 10.6%
Found	:	C 48.7;	H 6.0;	N 10.3%

Example 22.

Preparation of (4-dipropylamino-3,5-dinitrophenyl)-methylsulphilimium tosylsulphonate

(4-dipropylamino-3,5-dinitrophenyl)methyl N-tosylsulphilimine was stirred in sulphuric acid (20 ml) at room temperature until a homogeneous solution was formed (about 1 hour). The solution was then poured into crushed ice and immediately extracted with chloroform (to prevent decomposition of the sulphoxide). The tosylate salt was obtained as an orange oil after drying and evaporation of the solvent it solidified as a yellow solid upon trituration with acetone/petroleum ether 40—60. M.p. 138—140°C.

Analysis:

Calculated for $C_{20}H_{28}O_7N_4S_2$	:	C 48.0;	H 5.6;	N 11.2%
Found	:	C 44.9;	H 5.6;	N 11.7%

TABLE 1

Example	Compound	m.p. °C.	Analysis	
7	Diphenylsulphilydene-N′-ethylurea	133–135	Calculated for $C_{15}H_{16}ON_2S$ Found	: C 66.2; H 5.9; N 10.3% : C 66.3 ; H 5.9; N 10.3%
8	Diphenylsulphilydene-N′-dimethylurea	85–87	Calculated for $C_{15}H_{16}ON_2S$ Found	: C 66.2; H 5.9; N 10.3% : C 66.7; H 6.0; N 10.1%
9	Diphenylsulphilydene-N′-phenylurea	130–132	Calculated for $C_{19}H_{16}ON_2S$ Found	: C 71.3; H 5.0; N 8.8% : C 71.0; H 5.2; N 8.8%
10	Diphenylsulphilydene-N′-(3,4-dichloro-phenyl)urea	177–179	Calculated for $C_{19}H_{14}ON_2SCl_2$ Found	: C 58.7; H 3.6; N 7.2% : C 58.8; H 3.6; N 7.0%
11	Diphenylsulphilydene-N′-p-tosyl urea	178–180	Calculated for $C_{20}H_{18}O_3N_2S_2$ Found	: C 60.3; H 4.5; N 7.0% : C 59.6 ; H 4.5; N 6.8%
12	Diphenylsulphilydene-N′-phenylthiourea	116–118	Calculated for $C_{19}H_{16}N_2S_2$ Found	: C 68.0; H 4.8; N 8.3% : C 68.2; H 4.9; N 8.3 %
13	Diphenylsulphilydene-N′-propyl carbamate	70–72	Calculated for $C_{16}H_{17}O_2SN$ Found	: C 66.9; H 5.9; N 4.9% : C 68.1; H 6.0; N 4.9%
14	Diphenylsulphilydene-N′-thioethyl carbamate	84–86	Calculated for $C_{15}H_{15}OS_2N$ Found	: C 62.4; H 5.2; N 11.8% : C 62.8; H 5.2; N 11.7 %
15	N-(dimethoxythiophosphoryl)-diphenyl-sulphilimine	oil	Calculated for $C_{14}H_{16}O_2S_2NP$ Found	: C 52.1; H 5.0; N 4.3% : C 51.2; H 4.7; N 4.0%
16	N-(diethoxythiophosphoryl)-diphenyl-sulphilimine	oil	Calculated for $C_{16}H_{20}O_2NS_2P$ Found	: C 54.8; H 5.7; N 4.0% : C 54.0; H 5.5; N 3.7%

TABLE 1 (Continued)

Example	Compound	m.p. °C.	Analysis
17	N-(diphenoxyphosphoryl)-diphenyl-sulphilimine	oil	Calculated for $C_{24}H_{20}O_3NSP$: C 66.5; H 4.6; N 3.2% Found : C 66.8; H 4.6; N 3.0%
18	N-(2-nitro-4-trifluoromethylphenyl)diphenyl-sulphilimine	110–112	Calculated for $C_{19}H_{13}O_2N_2SF_3$: C 58.5; H 3.3; N 7.2% Found : C 58.2; H 3.4; N 7.0%
19	N-(2,6-dinitro p-tosyl)diphenyl sulphilimine	162–164	Calculated for $C_{19}H_{15}O_6N_3S_2$: C 53.2; H 3.7; N 9.8% Found : C 53.1; H 3.7; N 9.8%
20	N-(2,6-dinitro-4-trifluoromethylphenyl)-diphenyl sulphilimine	88–90	Calculated for $C_{19}H_{12}O_4N_3SF_3$: C 52.4; H 2.8; N 9.7% Found : C 52.2; H 2.8; N 9.4%

Example 23.

Preparation of (4-dipropylamino-3,5-dinitrophenyl)-methylsulphilydene-N'-methylurea

A mixture of (4-dipropylamino-3,5-dinitrophenyl)-methyl-sulphilimine (1.5 g) and methylisocyanate (0.15 g) was stirred in dry benzene for 5 minutes at room temperature. After evaporation of the solvent the product remained as an orange yellow solid (1.0 g). M.p. 160—162°C.

Analysis:

Calculated for $C_{15}H_{22}O_5N_5S$: C 46.8; H 6.0; N 18.2%
Found : C 47.2; H 6.1; N 17.8%

Example 24.

Preparation of (4-dipropylamino-3,5-dinitrophenyl)-methyltrichlororacetylsulphilimine

A chloroform solution of 2.0 g of the compound prepared according to Example 23 was treated with 10% sodium hydroxide solution. The chloroform solution was then separated, dried and evaporated. Trichloroacetylchloride (0.36 g) in benzene was added, and the mixture left at room temperature over night. It was filtered off the hydrochloride salt. The filtrate was subjected to evaporation to give the desired product as an orance semi-solid which completely solidified (0.8 g) upon trituration with acetone. M.p. 194—196°C.

Analysis:

Calculated for $C_{15}H_{19}O_5N_4SCl_3$	:	C 38.1;	H 4.0;	N 11.8%
Found	:	C 38.2;	H 4.3;	N 11.2%

Examples 25—33.

Following procedures similar to those given in previous Examples, further compounds were prepared, the physical characteristics and analyses are set out in Table 2.

Example 34.

Preparation of N-ethyl-N-tosyldimethyl-sulphilium tetrafluoroborate

Dimethyl-N-tosylsulphilimine (2.6 g) and Meerwein's reagent (1.9 g) were stirred in dry methylene chloride for 3 days. A colourless gum was obtained upon evaporation, which eventually set to a mass of oily crystals of the product (3.5 g), after trituration with ether/methylene chloride. M.p. 84—87°C.

TABLE 2

Example	Compound	m.p. °C.	Analysis
25	(4-Dipropylamino-3,5-dinitrophenyl)-methyl sulphilimium chloride	150–152	Calculated for $C_{13}H_{21}O_4N_4SCl$: C 42.9; H 5.3; N 15.4% Found : C 40.7; H 5.7; N 14.7%
26	(4-Dipropylamino-3,5-dinitrophenyl)-methyl-sulphilydene-N'-phenyl urea	130–132	Calculated for $C_{20}H_{25}O_5N_5S$: C 53.8; H 5.6; N 15.7% Found : C 46.8; H 5.1; N 13.5%
27	(4-Dipropylamino-3,5-dinitrophenyl)-methyl-sulphilydene-N'-(3,4-dichlorophenyl)urea	148–150	Calculated for $C_{20}H_{23}O_5N_5SCl_2$: C 46.6; H 4.5; N 13.6% Found : C 46.8; H 5.1; N 13.5%
28	(4-Dipropylamino-3,5-dinitrophenyl)-methyl-N-diphenoxyphosphoryl-sulphilimine	115–118	Calculated for $C_{25}H_{29}O_7N_4SP$: C 53.6; H 5.2; N 10.0% Found : C 52.7; H 5.2; N 10.0%
29	(4-Dipropylamino-3,5-dinitrophenyl)-methyl-N-cyano sulphilimine	155–157	Calculated for $C_{14}H_{19}O_4N_5S$: C 47.7; H 5.4; N 19.7% Found : C 48.0; H 5.8; N 19.4%
30	(4-Dipropylamino-3,5-dinitrophenyl)-methyl-N-tosylsulphilimine	148–150	Calculated for $C_{20}H_{26}O_6N_4S_2$: C 50.2; H 5.4; N 11.7% Found : C 50.3; H 5.7; N 11.9%
31	(4-Dipropylamino-3,5-dinitrophenyl)-methyl-N-phenylsulphonyl sulphilimine	179–181	Calculated for $C_{19}H_{24}O_6N_4S_2$: C 48.8; H 5.1; N 11.9% Found : C 49.1; H 5.1; N 11.8%
32	(4-Dipropylamino-3,5-dinitrophenyl)-N'-(2,2'-dicyanovinyl) sulphilimine	179–181 (dec)	Calculated for $C_{17}H_{20}O_4N_6S$: C 50.5; H 4.9; N 20.8% Found : C 50.0; H 5.1; N 20.6%
33	(4-Dipropylamino-3,5-dinitrophenyl)-methyl-N'-(1,2,2'-tricyanovinyl) sulphilimine	180–182	Calculated for $C_{18}H_{19}O_4N_7S$: C 50.4; H 4.4; N 22.8% Found : C 50.1; H 4.4; N 22.9%

Analysis:

Calculated for $C_{11}H_{18}O_2NS_2F_4B$	:	C 38.1;	H 5.2;	N 4.0%
Found	:	C 36.8;	H 5.0;	N 4.2%

Example 35.

Preparation of methyl-p-nitrophenylsulphilium mesitylene sulphonate

Methyl-(p-nitrophenyl)sulphide (3.38 g) and mesityl sulphonic acid (4.3 g) were stirred together in methylene chloride (30 ml) for 1¼ hours at room temperature. The off-white product (4.0 g) was obtained by the addition of excess ether. M.p. 132—134°C.

Analysis:

Calculated for $C_{16}H_{20}O_5N_2S_2$	:	C 49.9;	H 5.2;	N 7.3%
Found	:	C 50.5;	H 5.5;	N 7.3%

Examples 36—55.

Following procedures similar to those given in previous Examples, further compounds were prepared, the physical characteristics and analyses are set out in Table 3.

Example 56.

Preparation of methyl-(2-nitro-4-chlorophenyl)-N-tosylsulphilimine

(a) Methyl-2-nitro-4-chlorophenyl sulphide (2.04 g) and chloramine T (2.83 g) were suspended in methanol (150 ml) and acetic acid (0.5 ml) in methanol (5 ml) was added drop-wise, The mixture was then at 50°C for 0.5 hours, then cooled and poured into a dilute sodium hydroxide solution. The crude product was filtered off and recrystallised from acetone/petroleum ether 40—60 as off-white crystals (1.3 g). M.p. 188—190°C.

Analysis:

Calculated for $C_{14}H_{13}O_4N_2S_2Cl$	:	C 45.3;	H 3.2%	
Found	:	C 45.0;	H 3.5%	

(b) Using the same quantities as used in a) and using DMF as solvent, 2.85 g of the pure product was obtained directly by addition of excess water in the working-up procedure.

TABLE 3

Example	Compound	m.p. °C.	Analysis
36	(2-Nitro-4-chlorophenyl)-methyl sulphilimium hydrobromide	124–125 (dec)	Calculated for $C_7H_8O_2N_2SClBr$: C 28.6; H 2.7; N 9.5% Found : C 28.1; H 2.7; N 9.4%
37	N-Ethyl-N-tosyl-2-chloroethyl-methyl sulphilimium tetrafluoroborate	78–80	Calculated for $C_{12}H_{19}O_2NS_2ClF_4B$: N 3.5% Found : N 3.8%
38	N-Ethyl-N-tosyl-diethylsulphilimium tetrafluoroborate	gum	Calculated for $C_{13}H_{22}O_2NS_2F_4B$: C 41.6; H 5.9; N 3.7% Found : C 41.2; H 5.6; N 4.0%
39	N-Methyl-N-tosyl-2-chloroethyl-methyl-sulphilimium fluorosulphonate	140–142 (dec)	Calculated for $C_{11}H_{17}O_2NS_2ClF_4B$: C 33.5; H 4.3; N 3.6% Found : C 32.2; H 4.3; N 3.6%
40	2-Chloroethyl-methylsulphilimium mesitylene sulphonate	109–111	Calculated for $C_{12}H_{20}O_3NS_2Cl$: C 44.3; H 6.1; N 4.3% Found : C 44.7; H 6.3; N 4.3%
41	p-Chlorophenyl-methylsulphilimium mesitylene sulphonate	130–133	Calculated for $C_{16}H_{20}O_3NS_2Cl$: C 51.5; H 5.4% Found : C 50.8; H 6.2%
42	2-Chloro-4-nitrophenyl-methyl sulphilimium mesitylene sulphonate	165–167	Calculated for $C_{16}H_{19}O_5N_2S_2Cl$: C 45.9; H 4.5; N 6.7% Found : C 45.0; H 4.6; N 6.8%
43	Methyl-2-nitrophenylsulphilimium mesitylene sulphonate	100–104	Calculated for $C_{16}H_{20}O_5N_2S_2$: C 49.9; H 5.2; N 7.3% Found : C 47.1; H 5.2; N 6.3%
44	Methyl-(2-nitro-4-chlorophenyl) sulphilimium mesitylene sulphonate	183–185	Calculated for $C_{16}H_{19}O_5N_2S_2Cl$: C 45.9; H 4.5; N 6.7% Found : C 45.4; H 4.6; N 6.5%
45	Methyl-(2-nitro-5-chlorophenyl) sulphilimium mesitylene sulphonate	165–167	Calculated for $C_{16}H_{19}O_5N_2S_2Cl$: C 45.9; H 4.5; N 6.7% Found : C 45.7; H 4.7; N 6.5%

TABLE 3 (Continued)

Example	Compound	m.p. °C.	Analysis
46	2,6-Dinitrophenyl-methylsulphilimium mesitylene sulphonate	137–139	Calculated for $C_{16}H_{19}O_7N_3S_2$: C 44.8; H 4.4; N 9.8% Found : C 44.5; H 4.6; N 9.2%
47	2,4-Dinitrophenyl-methylsulphilimium mesitylene sulphonate	150–155	Calculated for $C_{16}H_{19}O_7N_3S_2$: C 44.8; H 4.4; N 9.8% Found : C 45.2; H 4.3; N 9.5%
48	2,4-Dinitro-6-chlorophenyl-methylsulphilimium mesitylene sulphonate	183–185	Calculated for $C_{16}H_{18}O_7N_3S_2Cl$: C 41.5; H 3.9; N 9.1% Found : C 41.9; H 4.0; N 8.5%
49	2-Formyl-4-nitrophenyl-methylsulphilimium mesitylene sulphonate	219–221	Calculated for $C_{17}H_{20}O_6N_2S_2$: N 6.8% Found : N 6.8%
50	Methyl-(2-nitro-4-trifluoromethyl) phenyl-sulphilimium mesitylene sulphonate	165–167	Calculated for $C_{17}H_{19}O_5N_2S_2F_3$: C 45.2; H 4.3; N 6.2% Found : C 44.8; H 4.3; N 6.1%
51	2,6-Dinitro-4-trifluoromethylphenylmethyl-sulphilimium mesitylene sulphonate	175–180	Calculated for $C_{17}H_{18}O_7N_3S_2F_3$: C 41.0; H 3.6; N 8.4% Found : C 42.0; H 4.2; N 7.9%
52	2-Cyano-3-chlorophenyl-phenylsulphimium mesitylene sulphonate	90–92	Calculated for $C_{22}H_{21}O_3N_2S_2Cl$: C 57.4; H 4.6; N 6.1% Found : C 57.0; H 4.4; N 5.8%
53	2-Cyano-3-chlorophenyl-p-tolyl-sulphilimium mesitylene sulphonate	142–144	Calculated for $C_{23}H_{23}O_3N_2S_2Cl$: C 58.2; H 4.9; N 5.9% Found : C 57.8; H 5.1; N 5.7%
54	p-Chlorophenyl-(2-cyano-3-chlorophenyl)-sulphilimium mesitylene sulphonate	143–145	Calculated for $C_{22}H_{20}O_3N_2S_2Cl_2$: C 53.4; H 4.0; N 5.7% Found : C 53.0; H 4.1; N 5.4%
55	p-Chlorobenzyl-(2-cyano-3-chlorophenyl)-sulphilimium mesitylene sulphonate	135–140	Calculated for $C_{23}H_{22}O_3N_2S_2Cl_2$: C 54.2; H 4.3; N 5.5% Found : C 53.8; H 4.3; N 5.2%

Example 57.

Preparation of p-(3,5-dinitrobenzoyloxy)phenyl-methyl-N-tosyl sulphilimine

(a) p-(3,5-Dinitrobenzoxy)phenyl methyl sulphide (3.34 g) and chloramine T (2.81 g) were suspended in methanol (200 ml) and acetic acid (0.5 ml) in methanol (5 ml) was added drop-wise. The mixture was stirred for 36 hours at 50°C, then filtered, and the crude product recrystallised from acetone/petroleum ether 60—80 and obtained as a colourless solid (1.5 g). M.p. 183—185°C.

Analysis:

Calculated for $C_{21}H_{17}O_8N_3S_2$	:	C 50.2;	H 3.4;	N 8.3%
Found	:	C 50.6;	H 3.6;	N 7.9%

(b) Using DMF as the solvent (800 ml) and warming at 50°C for just one hour, the sulphide (28.4 g) and chloramine T (23.9 g) in the presence of acetic acid (1 ml), yielded 35.5 g of the pure-off-white product directly upon adding excess water in the working-up procedure.

Examples 58—65.

Following procedures similar to those given in previous Examples, further compounds were prepared, the physical characteristics and analyses are set out in Table 4.

Example 66.

Preparation of N-(2,2'-dicyanovinyl)-methyl-3-nitrophenylsulphilimine

1.2 g of methyl-o-nitrophenylsulphilimine was stirred with ethoxymethylenemalononitrile in chloroform at room temperature for 3 hours. 0.5 g of a sandy coloured product was isolated by evaporation and trituration with acetone/petroleum ether 40—60 after 2 hours at room temperature. M.p. 185—187°C.

Analysis:

Calculated for $C_{11}H_8O_2N_4S$	:	C 50.7;	H 3.1;	N 21.6%
Found	:	C 50.5;	H 3.0;	N 21.4%

TABLE 4

Example	Compound	m.p. °C.	Analysis
58	2-Chloroethyl-methyl-N-tosyl-sulphilimine	113–115	Calculated for $C_{10}H_{14}O_2NS_2Cl$: C 42.9; H 5.0; N 5.0% Found : C 43.1; H 5.1; N 4.8%
59	2-Chloroethyl-methyl-N-phenyl-sulphonyl sulphilimine	175–178	Calculated for $C_9H_{12}O_2NS_2Cl$: C 40.6; H 4.7; N 5.5% Found : C 40.6; H 4.7; N 5.3%
60	p-(3,5-Dinitrobenzoyloxy)phenyl-methyl-N-phenyl sulphonyl sulphilimine	176–178	Calculated for $C_{21}H_{17}O_8N_3S_2$: C 49.1; H 3.1; N 8.1% Found : C 48.3; H 3.2; N 8.3%
61	p-Hydroxyphenyl-methyl-N-tosyl-sulphilimine	195–197	Calculated for $C_{14}H_{15}O_3NS_2$: C 54.4; H 4.9; N 4.5% Found : C 54.0; H 5.0; N 4.3%
62	Methyl-p-nitrophenyl-N-tosyl-sulphilimine	156–158	Calculated for $C_{14}H_{14}O_4N_2S_2$: C 49.7; H 4.1; N 8.3% Found : C 49.4; H 4.1; N 8.2%
63	4-Chloro-3,5-dinitrophenyl-methyl-N-tosyl-sulphilimine	210–212	Calculated for $C_{14}H_{12}O_6N_3S_2Cl$: C 40.2; H 2.9; N 10.0% Found : C 40.4; H 3.0; N 10.0%
64	2-Chloroethyl-phenylsulphonamido-N-phenyl-sulphonyl sulphilimine	96–98 (dec)	Calculated for $C_{14}H_{15}O_4N_2S_3Cl$: C 41.3; H 3.7; N 6.9% Found : C 41.2; H 3.5; N 6.0%
65	2,4-Dinitrophenyl-methyl-N-tosyl-sulphilimine	204–206	Calculated for $C_{14}H_{13}O_6N_3S_2$: C 44.0; H 3.1; N 11.0% Found : C 43.9; H 3.5; N 10.8%

Example 67

Preparation of methyl-2-nitrophenyl-N-(1,2,2'tricyanovinyl sulphilimine

1.0 g of methyl-o-nitrophenylsulphilimine was stirred with tetracyanoethylene in chloroform at room temperature. 0.9 g of the derived product was obtained as off-white, fluffy crystals. M.p. 189—190°C (dec).

Analysis:

Calculated for $C_{12}H_7O_2N_5S$:	C 50.0;	H 2.5;	N 25.0%
Found :	C 50.0%;	H 2.6%;	N 24.8%

Examples 68—71.

Following procedures similar to those given in previous Examples, further compounds were prepared, the physical characteristics and analyses are set out in Table 5.

Example 72.

Preparation of N-methyl-N'-(methyl-(2-nitro-4-chlorophenyl)sulphilydene) urea

0.2 g Methyl-(2-nitro-4-chlorophenyl)sulphilimine and 0.06 g methylisocyanate were stirred in benzene (20 ml) for 30 minutes at room temperature. The desired product was precipitated by the addition of petroleum ether 40—60. M.p. 165—167°C.

Analysis:

Calculated for $C_9H_{10}O_3N_3SCl$: C 39.2; H 3.6; N 15.2%
Found : C 38.9; H 3.7; N 14.9%

Example 73.

Preparation of N-cyano-methyl-(2-nitro-4-chlorophenyl)sulphilimine

2.18 g Methyl-(2-nitro-4-chlorophenyl)sulphilimine and cyanogen bromide (1.06 g) were stirred together in acetonitrile (20 ml) for 3 hours at room temperature. The mixture was filtered off the sulphilimine hydrobromide salt. The filtrate was subjected to evaporation. Silica chromatography of the residue with chloroform yielded 0.65 g of the pure sandy coloured product. M.p. 194—195°C (dec.).

TABLE 5

Example	Compound	m.p. °C.	Analysis
68	N-(2,2'-dicyanovinyl)-methyl-(2-nitro-5-chlorophenyl) sulphilimine	198–199 (dec)	Calculated for $C_{11}H_7O_2N_4SCl$: C 45.0; H 2.4; N 19.0% Found : C 44.6; H 2.4; N 18.6%
69	Methyl-(2-nitro-5-chlorophenyl)-N-(1,2,2'-tricyanovinyl) sulphilimine	208–210 (dec)	Calculated for $C_{12}H_6O_2N_5SCl$: C 45.1; H 1.9; N 22.0% Found : C 44.7; H 1.9; N 21.6%
70	N-(2,2'-dicyanovinyl)-methyl-(2-nitro-4-chlorophenyl) sulphilimine	200–202 (dec)	Calculated for $C_{11}H_7O_2N_4SCl$: C 45.0; H 2.4; N 19.0% Found : C 44.6; H 2.5; N 18.6%
71	Methyl-(2-nitro-4-chlorophenyl)-N-(1,2,2'-tricyanovinyl) sulphilimine	190–195 (dec)	Calculated for $C_{12}H_6O_2N_5SCl$: C 45.1; H 1.9; N 22.0% Found : C 45.2; H 2.0; N 21.4%

Analysis:
Calculated for $C_8H_6O_2N_3SCl$: C 39.6; H 2.5; N 17.3%
Found : C 39.7; H 2.6; N 17.2%

Example 74.

Preparation of methyl-(2-nitro-4-chlorophenyl) sulphilimine

(a) Methyl-2-nitro-4-chlorophenyl-N-tosylsulphilimine (2.0 g) was stirred in concentrated sulphuric acid (6 ml) for 15 minutes at room temperature. The black solution was poured into cold ether, and the resulting dark gum separated by decantation. The gum was dissolved in chlorform, washed with 10% sodium hydroxide solution, and the chloroform solution dried and evaporated to give the pure product as a bright yellow solid (0.4 g).

Analysis:
Calculated for $C_7H_7O_2N_2SCl$: C 38.4; H 3.2; N 12.8%
Found : C 38.3; H 3.3; N 12.2%

(b) Methyl-(2-nitro-4-chlorophenyl) sulphilimium mesitylene sulphonate (6.9 g) was dissolved in chloroform and stirred with 10% sodium hydroxide solution, and the chloroform solution dried and evaporated to yield the product (2.9 g). Also the following compounds were prepared in similar manners:

Example 75.
Methyl-(2-nitro-5-chlorophenyl) sulphilimine. M.p. 87—89°C.
Calculated for $C_7H_7O_2N_2SCl$: C 38.4; H 3.2; N 12.8%
Found : C 38.6; H 3.3; N 12.4%

Example 76.
Methyl-(2-chloro-4-nitrophenyl) sulphilimine. M.p. 64—66°C.
Calculated for $C_7H_7O_2N_2SCl$: C 38.4; H 3.2; N 12.8%
Found : C 37.8; H 3.3; N 11.6%

Example 77.
Methyl-O-nitrophenylsulphilimine. M.p. 78—79°C.

Calculated for $C_7H_8O_2N_2S$: C 41.6; H 5.0; N 13.8%
Found : C 41.8; H 4.6; N 13.8%

Example 78.

Preparation of N-ethyl-N-tosyldiphenylsulphilimium tetrafluoroborate

N-tosyldiphenylsulphilimine (3.55 g) and Meerwein's reagent (1.9 g) were stirred in dry methylene chloride (80 ml) for three days. The solvent was evaporated to yield a colourless oil, which eventually became crystalline (6.4 g) upon trituration with ether methylene chloride.

Analysis:
Calculated for $C_{21}H_{22}O_2NS_2F_4B$: C 53.6; H 4.7; N 3.0%
Found : C 53.5; H 5.0; N 3.3%

Example 79.

Herbicidal Activity

To evaluate their herbicidal activity, the sulphilimine derivatives were tested using as a representative range of plants:— maize, *Zea mays* (Mz); rice, *Oryza sativa* (R); barnyard grass, *Echinchloa crusgalli* (BG); oat, *Avena sativa* (O); linseed, *Linum usitatissium* (L); mustard, *Sinapsis alba* (M); sugar beet, *Beta vulgaris* (SB); and soya bean, *Glycine max* (S).

The tests fall into two categories, pre-emergence and post-emergence. The pre-emergence tests involved spraying a liquid formulation of the compound onto the soil in which the seeds of the plant species mentioned above had recently been

sown. The post-emergence tests involved two types of test, viz. soil drench and foliar spray tests. In the soil drench tests the soil in which seedling plants of the above species were growing, was drenched with a liquid formulation containing a compound of the invention, and in the foliar spray tests the seedling plants were sprayed with such a formulation.

The soil used in the tests was a steam-sterilised, modified John Innes Compost mixture in which half the peat, by loose bulk, had been replaced by vermiculite.

The formulations used in the tests were prepared by diluting with water solutions of the compounds, in acetone containing 0.4% by weight of an alkylphenol/ethylene oxide concentrate available under the trade name TRITON X-155 ("TRITON" is a Registered Trade Mark). In the soil spray and foliar spray tests the acetone solutions were diluted with an equal volume of water and the resulting formulations applied at dosage levels corresponding to 10 or 5 and 1 kilograms of active material per hectare respectively in a volume equivalent to 400 litres per hectare. In the soil drench tests one volume of the acetone solution was diluted to 155 volumes with water and the resulting formulation applied at one dosage level equivalent to 10 kilograms of active material per hectare in a volume equivalent to approximately 3000 litres per hectare.

In the pre-emergence tests untreated sown soil and in the post-emergence tests untreated soil bearing seedling plants were used as controls. The herbicidal effects of the compounds were assessed visually seven days after spraying the foliage and drenching the soil and eleven days after spraying the soil, and were recorded on a 0—9 scale. A rating 0 indicates no effect on the treated plants, a rating 2 indicates a reduction in fresh weight of stem and leaf of the plants of approximately 25%, a rating 5 indicates a reduction of approximately 55%, a rating 9 indicates a reduction of 95% etc.

The results of the tests are set out in the Tables 6—9.

Example 80.

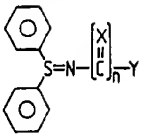
Insecticidal activity

The insecticidal activity of the sulphilimine derivatives was tested as follows:—

I. The compounds were formulated as solutions or suspensions in water containing 20% by weight of acetone and 0.05% by weight of TRITON X-100 as wetting agent. The formulations contained 0.7% by weight of the compound to be tested. Broad bean plants, trimmed to one leaf each, were sprayed on the undersurface of the leaf with the above formulation. Spraying was effected with a spraying machine delivering 450 litres per hectare, the plants passing under the spray in a moving belt. Ten apterous (6 day old) vetch aphids (*Megoura vicide*) were placed on the sprayed leaf of each broad bean plant. The plants were then enclosed in glass cylinders filled at one end with a muslin cap. Mortality counts were made after 24 hours.

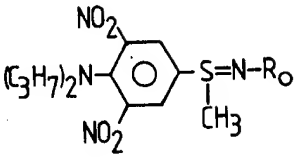
II. In tests against glass house spider mites (*Tetranychus urticus*) leaf discs cut from French bean plants were sprayed in the manner described under I. 1 hour after spraying, the discs were inoculated with 10 adult mites. Mortality counts were made 24 hours after inoculation.

TABLE 6



Compound of Example	n	X	Y	kg/ha	Post-emergence (plants)															Seeds								
					Soil drench 10 kg/ha								Foliar species								Pre-emergence							
					Mz	R	BG	P	L	M	SB	T	Mz	R	BG	P	L	M	SB	T	Mz	R	BG	P	L	M	SB	T
12	1	S	-NH⟨⬡⟩	5	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	5	3	0
				1																								
2	1	S	-NH⟨⬡⟩	5	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	4	0	–
				1																								
3	1	O	-O-CH$_2$⟨⬡⟩	5	0	0	0	0	0	0	0	0	0	0	0	2	4	2	1	1	0	0	0	0	0	0	0	–
				1																								
5	0	–	O ‖ – P – (OEt)$_2$	5	0	0	0	0	0	0	0	0	1	1	3	2	5	5	3	3	0	0	0	0	0	0	0	0
				1																								
17	0	–	O –P–(O-⬡)$_2$	5	0	0	0	0	0	0	0	0	0	0	1	2	3	4	2	0	0	0	0	0	0	0	0	0
				1									0	0	0	1	1	1	0	0								
6	0	–	NO_2 ⬡ NO_2	5	0	0	0	0	0	0	0	0	3	2	4	1	6	3	0	2	0	0	0	0	0	0	0	0
				1									0	0	0	0	2	0	0	0								
20	0	–	NO_2 ⬡-CF_3 NO_2	5	0	0	0	0	0	0	0	0	0	0	3	1	4	1	0	0	0	0	0	0	0	0	0	0

TABLE 7



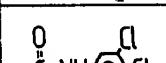
Compound of Example	R_o^{ϕ}	Dose kg/ha	Post-emergence (plants)														Seeds						
			Soil drench 10 kg/ha								Foliar species								Pre-emergence						
			Mz	R	GB	P	L	M	SB	T	Mz	R	BG	P	L	M	SB	T	Mz	R	BG	P	L	M	SB
25	H(HCl salt)	5	3	4	3	0	0	0	0	0	3	3	2	1	7	3	6	6	6	7	9	0	0	0	6
		1									0	0	0	0	4	1	0	2	0	4	7	0	0	0	0
22	H(tosylate)	5	4	6	4	0	0	0	0	0	3	0	3	0	6	5	1	1	6	8	9	0	3	0	0
		1									0	0	1	0	1	0	0	0	5	5	8	0	0	0	0
21	H(mesitylate)	5	0	0	0	0	0	0	0	0	5	2	4	5	4	3	2	1	1	7	9	0	0	0	3
		1									0	0	0	0	0	0	0	0	0	3	8	0	0	0	0
23	$-\overset{O}{\overset{\|}{C}}-NHCH_3$	5	1	5	4	0	0	0	0	0	3	0	0	0	5	3	0	0	7	8	8	0	0	0	0
		1									1	0	0	0	2	0	0	0	2	5	7	0	0	0	0
26		5	0	0	0	0	0	0	0	0	0	0	0	0	4	0	0	0	0	0	4	0	0	0	0
		1									0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
27		5	0	0	0	0	0	0	0	0	0	0	0	0	5	0	0	0	0	3	7	0	0	0	0
		1									0	0	0	0	1	0	0	0	0	0	0	0	0	0	0
24	$-\overset{O}{\overset{\|}{C}}-CCl_3$	5	5	1	4	0	0	0	0	0	4	0	0	0	5	0	0	3	5	5	9	0	0	0	0
		1									0	0	0	0	2	0	0	1	0	0	5	0	0	0	0

TABLE 7 (Continued)

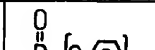
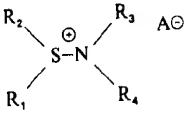
Compound of Example	R_o^{ϕ}	Dose kg/ha	Post-emergence (plants)																Seeds						
			Soil drench 10 kg/ha								Foliar species								Pre-emergence						
			Mz	R	GB	P	L	M	SB	T	Mz	R	BG	P	L	M	SB	T	Mz	R	BG	P	L	M	SB
28		5	0	0	0	0	0	0	0	0	2	0	0	2	4	0	2	2	1	3	8	0	0	0	0
		1									0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
29	– CN	5	3	3	7	0	0	0	0	0	3	0	6	0	1	0	0	0	1	5	8	2	4	0	3
		1									0	0	4	0	0	0	0	0	0	3	6	0	0	0	0
30		10	0	0	6	0	0	1	0	0	0	0	2	0	2	0	0	0	0	0	7	0	0	0	0
		1									0	0	0	0	0	0	0	0	0	0	2	0	0	0	0

TABLE 8



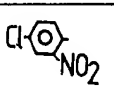
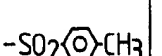
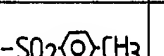
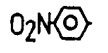
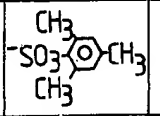
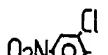
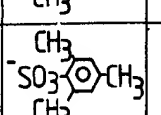
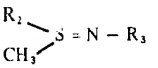
Compound of Example	R_2	R_1	R_3	R_4	A	Dose kg/ha	Post-emergence (plants)								Seeds						
							Foliar spray								Pre-emergence						
							Mz	R	GB	P	L	M	SB	T	Mz	R	GB	P	L	M	SB
36	CH_3		H	H	Br	5	3	2	6	1	8	9	8	6	0	4	0	0	0	0	0
						1	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
34	CH_3	CH_3	C_2H_5		BF_4	10	1	2	6	1	7	8	8	4	0	0	6	0	0	0	2
						1	0	0	1	0	1	0	1	4	0	0	8	0	0	0	0
38	C_2H_5	C_2H_5	C_2H_5		BF_4	10	0	1	6	1	7	6	8	2	0	0	0	0	0	0	0
						1	0	0	0	0	0	0	1	2							
35	CH_3		H	H		5	2	2	8	3	3	7	2	9	0	0	0	0	0	0	0
						1	0	0	4	1	0	1	0	2							
42	CH_3		H	H		5	1	1	5	0	0	0	0	0	0	0	0	0	0	0	0
						1	0	0	0	0	0	0	0	0							

TABLE 8 (Continued)

Compound of Example	R_2	R_1	R_3	R_4	A	Dose kg/ha	Post-emergence (plants) Foliar spray Mz	R	GB	P	L	M	SB	T	Seeds Pre-emergence Mz	R	GB	P	L	M	SB
43	CH_3		H	H		5	0	0	3	0	4	2	3	5	0	0	0	0	0	0	0
						1	0	0	0	0	0	0	1	0							
46	CH_3		H	H		5	1	0	5	1	2	2	0	3	0	0	0	0	0	0	0
						1	0	0	0	0	0	1	0	0							
47	CH_3		H	H		5	2	2	2	0	2	1	2	6	0	0	0	0	0	0	0
						1	0	0	0	0	0	0	0	2							
48	CH_3		H	H		5	0	0	0	1	1	4	3	0	0	0	0	0	0	0	0
						1	0	0	0	0	0	2	2	0	0	0	0	0	0	0	0
55			H	H		5	3	0	3	3	5	5	3	8	0	0	0	0	0	0	0
						1	0	0	0	0	0	0	0	0							

No Post-emergence soil drench activity.

TABLE 9



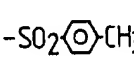
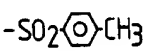
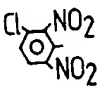
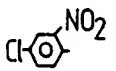
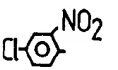
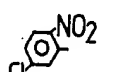
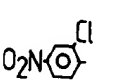
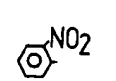
Compound of Example	R_2	R_3	Dose kg/ha	Post-emergence																Seeds									
				Soil drench 10 kg/ha								Foliar spray								Pre-emergence									
				Mz	R	GB	P	L	M	SB	T	Mz	R	BG	P	L	M	SB	T	Mz	R	BG	P	L	M	SB	T		
56			10 1	0	1	1	0	5	0	0	–	2 1	7 3	9 6	2 0	9 6	9 7	9 2	–	1	9	9 1	1	6	6	1	–		
62			10 1	0	0	0	0	0	0	0	0	0 0	0 0	0 0	0 0	4 0	0 0	0 0	0 0	0	0	0	0	0	0	0	0		
70		–CH=C(CN)$_2$	5 1	0	4	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	4	0	0	–		
67		–C(CN)=C(CN)$_2$	5 1	0	0	0	0	0	0	0	0	1 0	0 0	2 0	0 0	2 1	4 1	2 1	4 4	0 0	2 0	3 0	0 0	0 0	2 0	2 0	– 0		
66		–CH=C(CN)$_2$	5 1	0	0	0	0	1	2	1	1	3 0	0 0	3 0	1 0	6 3	6 4	3 1	5 4	0 0	4 1	5 1	0 0	4 0	3 1	2 1	– –		

TABLE 9 (Continued)

Compound of Example	R_2	R_3	Dose kg/ha	Post-emergence																Seeds								
				Soil drench 10 kg/ha								Foliar spray								Pre-emergence								
				Mz	R	GB	P	L	M	SB	T	Mz	R	BG	P	L	M	SB	T	Mz	R	BG	P	L	M	SB	T	
72		$-C(O)NHCH_3$	5	0	3	0	0	0	0	1	2	2	0	7	1	6	5	1	3	2	9	7	3	3	1	0	–
			1									0	0	1	0	1	2	0	0	0	0	0	0	0	0	0	–
74		H	5	0	3	0	0	1	0	0	0	3	1	8	3	8	9	8	8	3	9	9	3	8	7	3	–
			1									2	0	2	0	4	4	1	1	0	0	0	0	1	0	1	–
75		H	5	0	0	0	0	0	0	0	0	1	1	7	3	8	9	5	9	0	0	0	0	0	0	0	–
			1									0	0	2	1	3	1	4	1								
76		H	5	0	0	0	0	0	0	0	0	2	2	7	4	9	8	8	9	0	2	5	0	4	2	0	–
			1									1	0	1	2	1	3	2	3	0	0	0	0	0	0	0	–
77		H	5	0	1	1	1	3	3	3	2	4	3	8	4	9	9	5	9	0	8	3	2	2	2	0	–
			1									2	0	4	0	3	4	2	4	0	0	2	0	0	0	0	–

The results of the tests against vetch aphids (Mv) and spider mites (Tu) are shown in Table 10 in which 2 denotes greater than 80% kill, 1 50—80% kill and 0 less than 50% kill of the test species.

TABLE 10

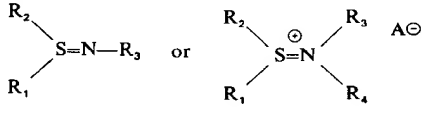
Compound of Example	Activity	
	M.v.	T.u.
74	1	0
77	0	1
70	0	0
67	0	0
68	1	0
69	2	1

Example 81.

The compounds described in the Examples 22, 24, 25, 26, 27 and 29 exhibited plant growth regulating activities, especially growth depression and thickening of stems as well as shortened internodes (in linseed).

WHAT WE CLAIM IS:—

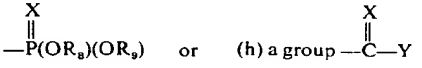
1. A method of controlling or eradicating pests at a locus which comprises applying to the pest or to the locus of the pest a pesticidally effective amount of a sulphilimine derivative of formula:



(I) (II)

wherein each of R_1 and R_2 independently represents an optionally substituted alkyl, cycloalkyl, aryl, aralkyl, alkaryl or sulphonamido group;

R_3 represents (a) a hydrogen atom when at least one of R_1 and R_2 does not represent a lower alkyl or phenyl group, (b) a trihaloacetyl group, (c) a cyano group when at least one of R_1 and R_2 represents an at least disubstituted phenyl group, (d) a phenyl group containing up to 4 substituents, (e) an optionally substituted benzene sulphonyl group provided that, when, in a derivative of formula I, this is a para-tosyl group, at least one of R_1 and R_2 represents a phenyl group having at least one non-alkyl substituent, or one of R_1 and R_2 represents a haloalkyl group and the other represents an alkyl group and when the benzene sulphonyl group has an optionally substituted amino substituent in the para position, at least one of R_1 and R_2 does not represent a lower alkyl or phenyl group, or (f) a group $—C(Q)=C(CN)_2$ when at least one of R_1 and R_2 represents a substituted phenyl group, (g) a group



in which

Q represents a hydrogen atom, a cyano group or an optionally substituted alkyl group;

X represents an oxygen or sulphur atom;

Y represents a group $-NR_5R_6$ or ZR_7, in which Z represents an oxygen or sulphur atom; each of R_5 and R_6 independently represents a hydrogen atom, or an optionally substituted alkyl, cycloalkyl, aryl, alkaryl, or aralkyl group; and R_7 represents an optionally substituted alkyl, cycloalkyl, aryl, aralkyl, or alkaryl group;

and each of R_8 and R_9 independently represents an optionally substituted alkyl, cycloalkyl, aryl, alkaryl, or aralkyl group;

R_4 represents a hydrogen atom, an optionally substituted alkyl, cycloalkyl, acyl or aryl sulphonyl group;

and A represents an anion.

2. A method as claimed in Claim 1, wherein, in the groups represented by Q, R_1, R_2, R_4, R_5, R_6, R_7, R_8 and R_9 in formulae I and II in Claim 1 the alkyl, alkaryl and aralkyl groups have up to 10 carbon atoms, and the cycloalkyl groups have from 5 to 8 carbon atoms.

3. A method as claimed in Claim 1 or 2 wherein in formulae I and II each of R_1 and R_2 independently represents an alkyl group optionally substituted by one or more halogen atoms; a benzenesulphonamido which may be substituted by up to 3 alkyl groups, or a cycloalkyl, phenyl, aralkyl or alkaryl group which may be substituted by one or more halogen atoms and/or alkyl, hydroxy, alkoxy, cyano, formyl, nitro, polyhaloalkyl, amino, or mono- or di-alkylamino groups or by a benzoyloxy group which may itself be substituted with up to 4 halogen atoms or nitro groups;

R_3 represents (a) a hydrogen atom, (b) a trihaloacetyl group, (c) a cyano group, (d) a phenyl group substituted by one or more halogen atoms, nitro groups, or amino, or mono- or di-alkylamino groups, (e) a benzene sulphonyl group (e') a para-tosyl group provided that at least one of R_1 and R_2 represents a phenyl group having at least one nitro substituent, or (f) a group $-C(Q)=C(CN)_2$ when at least one of R_1 and R_2 represents a phenyl group having at least one nitro substituent, or (g) a group

$$-\overset{\overset{X}{\|}}{P}(OR_8)(OR_9) \quad \text{or} \quad \text{(h) a group} -\overset{\overset{X}{\|}}{C}-Y$$

in which

Q represents a hydrogen atom, a cyano group or an alkyl group optionally substituted by one or more halogen atoms;

X represents an oxygen or sulphur atom;

Y represents a group $-NR_5R_6$ or $-ZR_7$ in which Z represents an oxygen or sulphur atom; each of R_5 and R_6 independently represents a hydrogen atom, an alkyl group optionally substituted by one or more halogen atoms, or a cycloalkyl, phenyl, alkaryl or aralkyl group optionally substituted by one or more halogen atoms and/or one or more alkyl, hydroxy, cyano, formyl, nitro, polyhaloalkyl, amino, or mono- di-alkylamino groups or by a benzoyloxy group which may itself be substituted by up to 4 halogen atoms or nitro groups; and R_7 represents an alkyl, cycloalkyl, phenyl, alkaryl or aralkyl group optionally substituted by one or more halogen atoms or a haloalkyl group;

and each of R_8 and R_9 independently represents an alkyl, cycloalkyl, alkaryl, or aralkyl group optionally substituted by one or more halogen atoms, alkyl or nitro groups;

R_4 represents a hydrogen atom, an alkyl or cycloalkyl group, an acyl group of up to 11 carbon atoms, or a benzene sulphonyl group which may be substituted by up to 3 alkyl groups;

and A represents a halide, polyhalide, (thio)carboxylate, cyanide, hydroxide, sulphate, alkylsulphate, hydrogen-sulphate, benzene sulphonate, alkyl- or alkylsubstituted benzene sulphonate, nitrate, phosphate, hydrogen phosphate, carbamate, mono- or dialkyl substituted carbamate, hydrogen carbonate, alkyl sulphonate, chlorate, perchlorate, bromate, perbromate, thiocyanate, tetrafluoroborate or thiosulphonate.

4. A method as claimed in Claim 1, wherein the sulphilimine derivative is a compound of formula I as defined in Claim 1 in which R_1 is a methyl group; R_2 is a

phenyl group substituted by one or more halogen atoms and/or nitro groups; and R_3 is a hydrogen atom.

5. A method as claimed in Claim 4 wherein R_2 represents a phenyl group substituted by one halogen atom and one nitro group.

6. A method as claimed in Claim 1 wherein the sulphilimine derivative is a compound of formula I in which:

R_1 and R_2 both represent phenyl groups; and

R_3 represents a trihaloacetyl group, a phenyl group substituted by up to 3 nitro, trifluoromethyl or methosulphate groups or one of the groups (g)

$$-\overset{X}{\overset{\|}{P}}(OR_8)(OR_9) \quad \text{or} \quad \text{(h)} \; -\overset{X}{\overset{\|}{C}}-Y$$

(in which Y is $-NR_5R_6$ or $-ZR_7$) and wherein;

R_5 represents a hydrogen atom or one of the groups represented by R_6;

R_6 represents an alkyl group of up to 6 carbon atoms, a cycloalkyl group of from 5 to 8 carbon atoms, or a phenyl group optionally substituted with one or two halogen atoms or one or two alkyl groups of up to 4 carbon atoms;

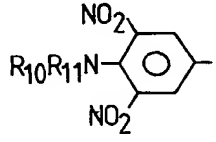
R_7 is an alkyl group of up to 6 carbon atoms or a phenyl or a benzyl group; and each of R_8 and R_9 independently represents an alkyl group of up to 6 carbon atoms or a phenyl group.

7. A method as claimed in Claim 6 wherein any cycloalkyl group represented by R_5 or R_6 is a cyclohexyl group, the optional substituents on any phenyl groups represented by R_5 or R_6 are chlorine or fluorine atoms, any alkyl groups represented by R_7 are ethyl or isopropyl groups, and when R_3 represents an optionally substituted phenyl group, that group is a 2,6-dinitrophenyl group.

8. A method as claimed in Claim 1 wherein the sulphilimine derivatives are compounds of formula I or II wherein

R_1 represents an alkyl group of up to 6 carbon atoms;

R_2 represents a group of formula:



wherein each of R_{10} and R_{11} independently represents an alkyl group of up to 6 carbon atoms;

R_3 represents (a) a hydrogen atom, (b) a trihaloacetyl group, (c) a cyano group, (e) a benzene sulphonyl group optionally substituted by up to 3 alkyl groups, or (f) the group $-C(Q)=C(CN)_2$, (g) the group

$$-\overset{X}{\overset{\|}{P}}(OR_8)(OR_9) \quad \text{or} \quad \text{(h) a group} \; -\overset{O}{\overset{\|}{C}}-NR_5R_6$$

in which,

Q represents a hydrogen atom, a cyano group, or an alkyl group of up to 6 carbon atoms;

X represents an oxygen or sulphur atom;

R_5 represents a hydrogen atom or a group represented by R_6;

R_6 represents an alkyl group of up to 6 carbon atoms or a phenyl group optionally substituted by 1 or 2 of halogen atoms or alkyl groups of up to 6 carbon atoms;

and each of R_8 and R_9 independently represents an alkyl group of up to 6 carbon atoms or a phenyl group;

R_4 represents a hydrogen atom, an alkyl group of up to 6 carbon atoms, an acyl group or a benzene sulphonyl group optionally substituted by up to 3 alkyl groups; and A represents a halide, tetrafluoroborate, or fluorosulphonate ion, or a

benzenesulphonate group optionally substituted by up to 3 alkyl groups.

9. A method as claimed in Claim 8 wherein R_1 is a methyl group; R_{10} and R_{11} are both propyl groups; in the groups represented by R_3, the trihaloacetyl group, (b), is a trichloroacetyl group, the alkyl substituents on the benzene sulphonyl group, (e), are methyl groups, and the substituents on any phenyl groups represented by R_5 or R_6 are chlorine atoms; the alkyl substituents on a benzene sulphonyl group represented by R_4 and a benzene sulphonate group represented by A are methyl groups; and the halide ion represented by A is a chloride ion.

10. A method as claimed in Claim 9 wherein the sulphilimine derivative is methyl-(3,5-dinitro-4-dipropylamino)sulphilimine, hydrochloride or the corresponding p-tosyl- or O-mesitylene sulphonyl salt.

11. A method as claimed in Claim 9 wherein the sulphilimine derivative is methyl-(3,5-dinitro-4-dipropylaminophenyl)-N-(N'-methylamido)sulphilimine.

12. A method as claimed in Claim 1 wherein the sulphilimine derivatives are compounds of formula II in Claim 1 wherein,

R_1 represents a haloalkyl group of up to 10 carbon atoms, or a phenyl group substituted by one or more of halogen atoms, alkyl groups of up to 4 carbon atoms, trifluoromethyl, nitro, amino, cyano and formyl groups;

R_2 represents an alkyl group of up to 10 carbon atoms, a phenyl group optionally substituted by one or two halogen atoms or alkyl groups of up to 4 carbon atoms, or R_2 represents a benzyl group optionally ring substituted by 1 or 2 halogen atoms and/or alkyl groups of up to 4 carbon atoms;

R_3 represents a hydrogen atom or an alkyl group of up to 10 carbon atoms;

R_4 represents a hydrogen atom, or a benzene sulphonyl group optionally substituted by up to 3 alkyl groups;

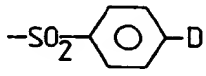
and A represents a halide, tetrafluoroborate, or fluorosulphonate ion, or a benzene sulphonium ion which may be substituted by up to 3 alkyl groups.

13. A method as claimed in Claim 12 wherein the haloalkyl group represented by R_1 is a 2-chloroethyl group; the halogen substituents on the phenyl group represented by R_1 are chlorine atoms; the halide ion represented by A is a chloride or bromide; and the alkyl substituents on the benzene sulphonyl group and benzene sulphonium ion, represented by R_4 and A respectively, are methyl groups.

14. A method as claimed in Claim 13 wherein the sulphilimine derivative is methyl-(p-nitrophenyl)-sulphilimine, O-mesitylene sulphonic acid salt.

15. A method as claimed in Claim 1 wherein the sulphilimine derivative is a compound of formula I wherein R_1 represents a haloalkyl group of up to 10 carbon atoms, or a phenyl group substituted by one or more halogen atoms, hydroxy, nitro or 3,5-dinitrobenzoyloxy groups;

R_2 represents an alkyl group of up to 6 carbon atoms; and R_3 represents a group of formula:



wherein D represents a hydrogen atom or an alkyl groups of up to 6 carbon atoms.

16. A method as claimed in Claim 15 wherein the haloalkyl group represented by R_1 is a 2-chloroethyl group; R_2 represents a methyl group; and the alkyl group; represented by D is a methyl group.

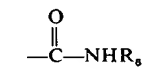
17. A method as claimed in Claim 15 wherein the sulphilimine derivative is methyl-(2-nitro-4-chlorophenyl)-N-(p-tolylsulphonyl)sulphilimine.

18. A method as claimed in Claim 1 wherein the sulphilimine derivative is a compound of formula I wherein:

R_1 represents a methyl group;

R_2 represents a 2-nitrophenyl group or a 2-nitrophenyl group substituted by a halogen atom; and

R_3 represents a group $-C(Q)=C(CN)_2$ or a group



in which Q represents a hydrogen atom, a cyano group or an alkyl group of up to 6 carbon atoms, and R_6 represents an alkyl group of up to 6 carbon atoms.

19. A method as claimed in Claim 18 wherein the halogen substituent in the 2-nitrophenyl group represented by R_2 is a chlorine atom; and the alkyl groups represented by Q and R_6 are methyl groups.

20. A pesticidal composition comprising as active ingredient at least one sulphilimine derivative of formula I or II as defined in any of the preceding claims together with a surface active agent and a carrier, provided than when R_3 is an optionally substituted benzene sulphonyl group substituted by a chlorine atom, a nitro or lower alkyl group, at least one of R_1 and R_2 is not an optionally substituted lower alkyl group, or a phenyl, benzyl or sulphonamido group.

21. A sulphilimine derivative of formula I or II in Claim 1 as defined in any of Claims 1 to 19 provided that:

(i) when R_3 represents a hydrogen atom, R_1 and R_2 do not both represent 4-fluorophenyl groups, nor both represent 4-chlorophenyl groups, neither R_1 nor R_2 represents a phenyl group or a 4-methylphenyl group, and when one of R_1 and R_2 represents a methyl group the other does not represent an octyl or tetradecyl group.

(ii) when R_3 represents a trihaloacetyl group, (b), R_1 and R_2 do not both represent lower alkyl groups, and if one of R_1 and R_2 represents a phenyl group, the other does not represent a methoxyphenyl group.

(iii) when R_3 represents a phenyl group, (d), that group contains from 2 to 4 substituents which are not 2,4- or 3,5-dinitro substituents, and at least one of R_1 and R_2 is not a lower alkyl group.

(iv) when R_3 represents an optionally substituted benzene sulphonyl group, (e), at least one of R_1 and R_2 represents an at least disubstituted phenyl group, other than a 2,4-dichlorophenyl group.

(v) when R_3 represents a group $—C(Q)=C(CN)_2$, (f), and Q represents a cyano group, R_1 and R_2 do not both represent phenyl groups.

(vi) when R_3 represents a group

—C—Y, (h), and this group is a lower alkoxycarbonyl group, neither R_1 nor R_2 represents a lower alkyl group.

(vii) when R_3 represents the group

—C—Y, (h), and this group is a methoxycarbonyl, ethoxycarbonyl, lower alkylaminocarbonyl, phenylamino carbonyl or phenylaminothioxomethyl group, R_1 and R_2 do not both represent phenyl groups.

(viii) when R_3 represents the group

—C—Y, (h), and this is an unsubstituted aminocarbonyl group, at least one of R_1 and R_2 is an at least disubstituted phenyl group.

22. A sulphilimine derivative as claimed in Claim 21 substantially as hereinbefore described with specific reference to any one of the Examples 2 to 6, 8, 10, 11, 13 to 18, 20, 24, 26—34, 36—55, 63 and 66—78.

23. A process for the preparation of compounds as claimed in Claim 21 or Claim 22 which comprises reacting a sulphide compound of formula R_1R_2S, wherein R_1 and R_2 have the meanings defined in Claim 21 with a compound of formula $MsONH_2$, wherein Ms represents a mesitylene sulphonyl group, or with a compound of formula TsNClNa, wherein Ts represents a tosyl group, and converting the sulphilimine of formula $R_1R_2S=NH$ or a salt thereof obtained into the desired sulphilimine of formula I or II.

24. A process as claimed in Claim 23 wherein the reaction between the sulphide and the mesitylene sulphonyl or tosyl-derivative is carried out in methanol or dimethylformamide in the presence of a small amount of a carboxylic acid.

25. A process for the preparation of sulphilimine derivatives as claimed in Claim 21 and defined with reference to Claim 6 or 7 which comprises reacting a diphenylsulphilimine with the appropriate (thio)isocyanate, or a compound of formula YCOCl or a compound of formula

$$Cl—\overset{\overset{X}{\|}}{P}(OR_6)(OR_9)$$

wherein Y, X, R_6 and R_9 are as defined in Claim 21 and with reference to Claim 6 or 7.

26. A process for the preparation of sulphilimine derivatives as claimed in Claim 21 and having formula I wherein R_3 represents a 2,6-dinitrophenyl- or a 2,6-dinitro-4-trifluoromethylphenyl- group by reacting a sulphilimine derivative of formula $R_1R_2S=NH$, wherein R_1 and R_2 are as defined in Claim 21, with the appropriate substituted chlorobenzene.

27. A sulphilimine derivative as claimed in Claim 21 when prepared by a process as claimed in any of Claims 23 to 26.

28. A method as claimed in any of Claims 1 to 19 wherein the pest is an unwanted plant, or unwanted plant growth.

29. A pesticidal composition as claimed in Claim 20 which is suitable for use as a herbicide.

30. A herbicidal composition as claimed in Claim 29 as hereinbefore described with specific reference to Example 79.

31. A pesticidal composition as claimed in Claim 20, suitable for use as an insecticide, and as described hereinbefore, with specific reference to Example 80.

32. A method as claimed in Claim 28 as described hereinbefore with specific reference to Example 79.

ROY C. ROGERS,
Chartered Patent Agent,
Shell Centre,
London, SE1 7NA.
Agent for the Applicants.

Printed for Her Majesty's Stationery Office by the Courier Press, Leamington Spa, 1981.
Published by the Patent Office, 25 Southampton Buildings, London, WC2A 1AY, from which copies may be obtained.